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*Semiconductor Measurement Technology:*

**Improved Infrared Response  
Technique for Detecting Defects and  
Impurities in Germanium and  
Silicon *p-i-n* Diodes**

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## Semiconductor Measurement Technology:

# Improved Infrared Response Technique for Detecting Defects and Impurities in Germanium and Silicon *p-i-n* Diodes

A. H. Sher

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A. H. Sher

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## PREFACE

The Semiconductor Technology Program serves to focus NBS efforts to enhance the performance, interchangeability, and reliability of discrete semiconductor devices and integrated circuits through improvements in measurement technology for use in controlling device fabrication processes and in specifying materials and devices in national and international commerce. Its major thrusts are the development of carefully evaluated and well documented test procedures and associated technology, for use on production lines and in the exchange of devices and materials, and the dissemination of such information to the electronics community. Application of the output by industry is expected to contribute to higher yields, lower cost, and higher reliability of semiconductor devices. In addition, the improvements in measurement technology will lead to greater economy in government procurement and will provide a basis for controlled improvements in fabrication processes and in essential device characteristics.

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SEMICONDUCTOR MEASUREMENT TECHNOLOGY:  
IMPROVED INFRARED RESPONSE TECHNIQUE FOR DETECTING DEFECTS  
AND IMPURITIES IN GERMANIUM AND SILICON *p-i-n* DIODES\*

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An infrared response (IRR) technique was evaluated for its utility in qualifying germanium for radiation detector use. Because of several improvements in the sensitivity and interpretation of the technique made during the evaluation, it was possible to observe a number of discrete energy levels lying within the forbidden energy gap of germanium which had passed unobserved in previous studies. These levels correlate with the type of defects and vacancies introduced by radiation damage into germanium as measured using such techniques as photoconductivity and Hall effect measurements after irradiation. Furthermore, the improved infrared response measurement method was used to identify impurities, such as copper, gold, and iron, and dislocations resulting from heat treatments in germanium. A major advance was made when it was determined that the IRR spectra could be grouped into five distinct types on the basis of spectral features observed in the energy range from 0.6 to 0.7 eV. One of the spectrum types represented crystals from which good quality detectors could be fabricated; the other four represented crystals that yielded poorer quality detectors due to carrier trapping, or crystals that presented problems such as low lithium drift mobility in detector fabrication. Three of the four spectrum types representative of poor crystal quality could be duplicated by suitably degrading specimens of a good quality crystal. The material and detector characteristics of crystals within each spectrum type were found to be similar.

*Key Words:* Carrier trapping; gamma-ray detector; germanium; Ge(Li) detector; infrared response; silicon.

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## 1. INTRODUCTION

Armantrout introduced a method that made use of the response of *p-i-n* diodes to monochromatic infrared radiation to identify trapping centers in material intended for use in fabricating Ge(Li) detectors [1]. Further investigation of this infrared response (IRR) technique was undertaken in order to corroborate the previously published findings and determine the applicability of the method. In the process, modifications were made that enhanced the sensitivity and scope of the measurement. This is manifested by increased observation of details in the IRR spectra and led to a better interpretation of energy levels arising from impurities and defects in both germanium and silicon crystals.

## 2. INITIAL MEASUREMENTS

In the IRR measurement, photons incident on a reverse-biased *p-i-n* diode induce the formation of free carriers in the depleted region of the device by excitation of carriers into or out of energy levels within the band gap. The current due to the generation of free carriers and the subsequent transport of these carriers to the electrodes of the diode is measured as a function of the incident photon energy. The diodes used in this study were, in most cases, lithium-drifted germanium gamma-ray spectrometer structures. These structures are produced by first thermally diffusing lithium, a donor impurity, into single crystal *p*-type germanium doped with an acceptor impurity, usually gallium. The resulting *p-n* junction is reverse-biased so that the mobile lithium ions drift into the crystal under the influence of the applied field. The lithium-ion donors compensate the charge of the acceptors present and produce a compensated region that contains few free charge carriers. This compensated or depleted region, sandwiched between the *n*-type diffused layer and remaining bulk *p*-type crystal, is sensitive to radiation. Figure 1 shows IRR spectra obtained from four lithium-compensated *p-i-n* germanium diodes using apparatus similar to that used in the original work [1] except that a grating (rather than a prism) monochromator and a phase-sensitive amplifier were employed [2]. The results are similar to those previously observed. Diodes NBS 83-3 and NBS 83-4 were fabricated from specimens of the same *p*-type germanium single crystal; the former was subjected only to the typical lithium-drifted detector fabrication process while the latter was, in addition, heated to 800°C and quenched to room temperature. Diodes NBS 13 and NBS 13Cu were fabricated from specimens of a germanium crystal with an initially high dislocation density ( $10^4 \text{ cm}^{-3}$ ). Diode NBS 13Cu was also doped with electrically active copper to a density of approximately  $1 \times 10^{14} \text{ cm}^{-3}$ . All that could be inferred from the IRR spectra of the four diodes on the basis of the previous studies [1] is that all the diodes except diode NBS 83-3 would show some degree of carrier trapping due to their observed response below approximately 0.7 eV and that diode NBS 13 exhibits the lithium-defect interaction as manifested by the shelflike response at 0.50 eV.

Considerably more information was obtained by improving the apparatus used to measure diode IRR by using 1-mm thick germanium filter windows

rather than the 3 to 4-mm thickness previously used. Figure 2 shows the IRR spectrum of diode NBS 83-3 obtained using the improved IRR technique; for the first time in this type of measurement the spectrum exhibits features which can be attributed to discrete levels rather than a continuum of states within the band gap as previously observed [1]. Assuming that the features indicated in figure 2 correspond to actual transitions into or out of energy levels within the band gap, the level scheme that can be constructed is in general agreement with those obtained from measurements of photoconductivity on radiation-damaged germanium [3].

The IRR spectra for the four diodes described above obtained using a 1-mm-thick germanium filter window are shown in figure 3. In contrast to the spectra in figure 1, those shown in figure 3 permit more positive identification of the origins of the spectral features. For example, the features in the spectrum of diode NBS 13Cu at 0.38 and 0.49 eV, corresponding to the known energy levels related to the presence of copper at 0.33 eV above the valence band and 0.22 eV below the conduction band, respectively [4], confirm the presence of that impurity in the test diode. The spectrum exhibited by diode NBS 83-4, the heat-treated specimen, is in agreement with a recent photoconductivity study [5] of the acceptor levels in germanium caused by plastic deformation which showed a broad spectral response corresponding to a continuum of states extending from approximately 0.4 to 0.6 eV, with a peaked response at 0.58 eV.

The peak at 0.36 eV (one-half the bandgap energy) shown in all the spectra in figure 3 is thought to arise from higher-order diffracted radiation present in the monochromator; peaks also observed at energies of 0.24 and 0.18 eV corresponding to one-third and one-quarter of the bandgap, respectively, seem to bear this out.

### 3. MECHANISM FOR DIODE IMPURITY PHOTOVOLTAGE (IRR)

A review of the literature on measurements of energy levels arising from the presence of defects and impurities in semiconductors by photoconductivity and related techniques has suggested that the steady-state photo-EMF, or photovoltage, established when minority carriers are generated by illumination is probably the basic mechanism for the IRR in *p-i-n* diodes with wide *i*-regions [6]. Figure 4 illustrates possible models whereby a photovoltage due to light in the impurity region (with energy less than the bandgap energy) can be observed in a diode near liquid nitrogen temperature, 77 K.

As shown in figure 4a, excitation by light in the impurity region can lead to optical transitions from the valence band,  $E_V$ , to an energy state which is empty or only partially occupied by electrons at equilibrium [7]. Double-optical transitions can also occur, as shown in figure 4b, where light transfers electrons from filled states to the conduction band,  $E_C$ . The equilibrium between these energy states and the valence band is upset and can be reestablished by subsequent optically-induced transitions from  $E_V$  to these states. Double-optical transitions are possible only if the energy of the exciting light is greater than one-half of the forbidden energy gap [7]. Furthermore, excitation with light of energy near the bandgap energy can produce "overpopulation" (charge exchange) of impurity or defect states which may lead to the

generation of a photovoltage. This is illustrated in figure 4c which represents the equilibrium energy level scheme of a semiconductor containing three levels in the forbidden gap. Upon illumination with light of energy equal to or greater than the bandgap energy (figure 4d) the electrons and holes produced by such excitation are captured by different states. Nonequilibrium electrons from the conduction band may be captured by level III establishing a steady-state population. Then holes may be captured by both level II and level III [8].

That the above photovoltage effects are responsible for the diode IRR is supported by the following observations made on germanium diodes [6,9] and confirmed in work with silicon. Firstly, no spectral features that can be linked to impurity or defect states have been seen at incident photon energy less than one-half the bandgap energy. Secondly, the IRR spectrum exhibits evidence of many discrete levels when a thin semiconductor filter is used. Thinner filters transmit more radiation of energy near the bandgap energy than do thicker filters.

Even though the photovoltage is only observed at energies greater than one-half the bandgap energy, it is possible to observe energy states which lie in both halves of the forbidden gap. The photovoltage is observed if the photon energy exceeds the energy difference between the state through which excitation is occurring and the edge of the conduction or valence band, whichever is greater [8].

#### 4. IRR MEASUREMENTS ON GERMANIUM

Infrared response measurements were carried out on two high-purity germanium detectors in which lithium-compensation was not used. Figure 5 shows IRR spectra obtained from these two high-purity diodes [10] and also from lithium drifted diode NBS 83-3. Diode NBS 112 was fabricated from a crystal with an initial net donor concentration of approximately  $7 \times 10^{10} \text{ cm}^{-3}$ . Relative to diode NBS 83-3, diode NBS 112 exhibits a conspicuous lack of structure in the spectrum between 0.50 and 0.54 eV, presumably because of the absence of lithium.

Diode NBS 113, the other high purity specimen, was intentionally doped with gold to a density of approximately  $10^{11} \text{ cm}^{-3}$ . Gold is known to introduce three acceptor levels in germanium located 0.05 eV and 0.15 eV above the valence band and 0.20 eV below the conduction band, and a donor level 0.04 eV below the conduction band [4]. The spectrum of diode NBS 113 shown in figure 5 shows evidence for the presence of levels at 0.57 eV (0.15 eV above the valence band), 0.66 eV (0.05 eV above the valence band), and 0.52 eV (0.20 below the conduction band).

Diode NBS 301 was fabricated from a crystal pulled from a melt which was contaminated with a chunk of stainless steel [11]. Levels in germanium arising from iron impurity are at energies of 0.34 eV above the valence band and 0.27 eV below the conduction band [4], and chromium introduces levels extending from 0.07 to 0.12 eV above the valence band [4]. The IRR spectrum of diode NBS 301 shown in figure 6 is interpreted to confirm the presence of these impurities by virtue of the incompletely resolved peak at 0.37 eV (iron level at 0.34 eV above the valence band)

shown in the inset and the "smearing" of the spectrum in the region extending from about 0.64 to 0.59 eV (chromium levels) relative to the spectrum of diode NBS 83-3. Diode NBS 83-6, whose spectrum is also shown in figure 6, was fabricated from a specimen of the same crystal as diode NBS 83-3, but after the lithium diffusion it was stored at room temperature for several months, resulting in lithium precipitation during the storage period. Lithium precipitate clusters would induce strain in the crystal lattice giving rise to a band of energy levels [1]. This is believed to account for the smoothing out of the IRR spectrum of diode NBS 83-6 relative to that of diode NBS 83-3.

While IRR spectra for lithium-drifted diodes with similar measured detector trapping characteristics may not be completely identical, the following comments can be made from a study of the spectra. In diodes which exhibit preferential electron trapping, the level at 0.50 eV is always observed in the IRR spectrum. This level corresponds to the lithium-defect trap located 0.21 eV below the conduction band which has been found to be an electron trap [1]. Figure 7 shows IRR spectra obtained from four lithium-drifted diodes two of which (diodes NBS 88 and NBS 303) exhibit marked electron trapping.

In diodes which exhibit preferential hole trapping (diodes NBS 74 and NBS 76), the level at 0.50 eV is not observed. The IRR spectra of this type of diode show a response that increases smoothly from 0.40 eV, peaks at about 0.56 eV and decreases to a valley near 0.59 eV.

The IRR spectrum resulting from neutron-irradiation of germanium was also studied for two diodes fabricated from specimens of the same crystal [12]. The portion of the crystal from which diode NBS 83-8 was fabricated had been irradiated with neutrons to a fluence of approximately  $1.3 \times 10^{10} \text{ cm}^{-2}$ . The IRR spectra of the two diodes, NBS 83-3 and NBS 83-8, are shown in figure 8. It is evident that features in the spectrum of diode NBS 83-8 at energies of 0.55, 0.61, and 0.63 eV are enhanced over those in the spectrum of diode NBS 83-3. The other features of the spectrum of diode NBS 83-3 appear to be preserved in the spectrum of diode NBS 83-8.

In studying radiation-damaged material, possible annealing effects must be considered. A published study of high-temperature annealing of defects produced by neutron irradiation of germanium [13] at fluences in the range  $10^{15}$  to  $10^{16} \text{ cm}^{-2}$  is particularly appropriate to the present case as the temperature range studied includes the temperatures employed in the fabrication process for lithium-drifted diodes. After irradiation, four energy states were reported, located at 0.01, 0.07, and 0.17 eV above the valence band and 0.20 eV below the conduction band. After annealing, a new level 0.10 eV below the conduction band was observed. With the exception of the state located 0.01 eV above the valence band which is not within the energy range shown in figure 8, these states correspond to the features labeled in the figure.

#### 4.1 IRR SPECTRUM TYPES

A study of infrared response spectra obtained from lithium-drifted germanium detectors showed that spectra observed to date can be grouped

into five types: one representative of good quality detectors and four representative of poor quality detectors [14].

Figure 9 shows a comparison of IRR spectra obtained from five Ge(Li) detectors fabricated from crystals from five different suppliers [curves (1) through (5)] with spectra obtained from four specimens of one crystal, each treated in a different manner [curves (A) through (D)]. From previous studies and a review of pertinent literature, it has been concluded that, in general, the energy region covered in figure 9, 0.57 to 0.70 eV, is that in which crystalline imperfections are detected; most of the features of these spectra arising from impurities fall below 0.57 eV in the IRR measurements. The spectra of these detectors exhibit distinct features that serve as the basis for dividing IRR spectra into the five types. The characteristics of each type of IRR spectrum are given in table 1.

Table 1 - Characteristics of Infrared Response Spectrum Types

Spectrum <sup>a</sup>	Energy Position of Minimum (eV)	Energy Position of Major Features (eV)	Comments
(1), (A)	0.66	0.65, 0.64, 0.63, 0.61, 0.59, 0.58	Rises sharply into bandedge above 0.66 eV.
(2), (B)	0.65	0.63, 0.61	Rises sharply into bandedge above 0.65 eV.
(3), (C)	0.68	0.66, 0.65, 0.64	Rises into bandedge above 0.68 eV; spectrum decreases below 0.66 eV.
(4), (D)	----	0.67, 0.66, 0.65	No prominent minimum; this type shows the least number of spectrum features (fairly featureless from 0.58 to 0.65 eV).
(5)	0.66	0.65, 0.63, 0.61	Small minimum; sharply rises into bandedge above 0.66 eV.

<sup>a</sup> as shown in figure 9

Table 2 summarizes some of the measured material and detector characteristics of the diodes studied. Of particular interest are the four reference diodes, whose IRR spectra are shown on the left side of figure 9. Each reference diode spectrum is set opposite the spectrum type on the right for which similar features are shown. The reference diodes were all fabricated from specimens of germanium crystal NBS 83, and the treatments to which they had been subjected, previously detailed, are summarized in table 2. Diode 83-4 (Spectrum D in figure 9) was heated to 800°C, quenched to room temperature, and is thought to contain approximately  $10^{14} \text{ cm}^{-3}$  thermal defects [15]. That the IRR spectrum of a germanium specimen of known high quality can be modified by specific treatment of

a crystal to yield spectra similar to that of lesser quality crystals as shown in figure 9, indicates for the first time that the energy region from about 0.57 to 0.70 eV can be used to yield qualitative information on crystalline imperfections in germanium.

Table 2 - Summary of Crystal and Diode Characteristics of Germanium Specimens

Spectrum <sup>a</sup>	Diode No.	Material Properties	Detector Properties	Corresponding Reference Diode	Spectrum <sup>a</sup>
(1)	NBS 619	Oxygen conc.: $< 10^{14} \text{ cm}^{-3}$	Good diode, slight electron trapping	NBS 83-3: lithium drift only, good detector	(A)
(2)	NBS 76	High Li mobility	Good diode, severe hole trapping	NBS 83-8: neutron-irradiated	(B)
(3)	NBS 91	Low Li mobility, oxygen conc.: $8 \times 10^{14} \text{ cm}^{-3}$	---	NBS 83-6: lithium precipitates	(C)
(4)	NBS 13	High Li mobility, high dislocation density	Very unstable, diode could not be maintained	NBS 83-4: thermal defects	(D)
(5)	NBS 302	---	Poor diode, electron trapping	---	

<sup>a</sup> as shown in figure 9.

Of 48 diodes studied, 25 percent exhibited spectra corresponding to that of a good quality gamma-ray detector, type (1). The remainder exhibited spectra of types thought to correspond to detectors of poorer quality: 38 percent like type (2); 12 percent like type (3); 4 percent like type (4); and 21 percent like type (5). Nearly four-fifths of the poorer quality diodes examined fell into types (2) and (5) [16].

Table 3 summarizes the measured material characteristics common to most of the diodes found in each representative group. These characteristics are generally similar to those of the diodes listed in table 2. It is interesting to note that the crystals yielding the poor quality detectors can be grouped, on the basis of the IRR spectra, into groups representative of two of the major detector problem areas: trapping of one of the charge carriers or poor lithium drift mobility. The problem of poor diode characteristics (reverse leakage current as a function of bias voltage) does not appear to be separately differentiated by IRR. Of course, carrier trapping and poor diode characteristics are

interrelated; if a sufficient field cannot be applied to the device, charge carriers may be trapped before being collected.

Problems manifested by crystals that exhibit IRR spectrum types (3) or (4) seem to be related to either the lithium-oxygen interaction or high dislocation density, respectively. With regard to carrier trapping, identified with spectrum types (2) and (5), the problem is more complex. The origin of spectrum type (5) has not been identified. Spectrum type (2) is characteristic of the neutron-irradiated reference diode, but it is not possible at present to link the defects known to be produced in germanium by neutron irradiation directly with the defects that produce IRR spectra of this type in the test crystals.

Table 3 - Material Properties of Lithium-Drifted Germanium Detectors

Spectrum Type	Dislocation Density	Oxygen Density	Lithium Mobility
1	<2500 cm <sup>-2</sup>	<2 × 10 <sup>14</sup> cm <sup>-3</sup>	High
2	<3500 cm <sup>-2</sup>	<3 × 10 <sup>14</sup> cm <sup>-3</sup>	High
3	>5000 cm <sup>-2</sup>	>5 × 10 <sup>14</sup> cm <sup>-3</sup>	Low
4	>10 <sup>4</sup> cm <sup>-2</sup>	>1 × 10 <sup>13</sup> cm <sup>-3</sup>	High
5	2500-8000 cm <sup>-2</sup>	<2 × 10 <sup>14</sup> cm <sup>-3</sup>	High

## 5. IRR MEASUREMENTS ON SILICON

Concurrent with the IRR study of germanium, IRR work on silicon nuclear radiation detectors was carried out [6,12]. The results of these measurements, mainly from radiation-damage experiments, were used to support the interpretation of IRR results on germanium.

Figure 10 shows IRR spectra obtained for a lithium-drifted silicon detector before and after irradiation with fast neutrons through the *p*-contact to a fluence of  $5 \times 10^9$  cm<sup>-2</sup> [12]. As might be expected for such a fluence the two spectra are nearly the same. However, the peaks at 0.86 and 0.77 eV are somewhat enhanced, and the feature at 0.93 eV is much enhanced after irradiation. The two lower energy peaks are associated with levels located 0.40 eV below the conduction band (0.77 eV) and 0.31 eV above the valence band (0.86 eV). Such levels have been previously reported from observations of photoconductivity on silicon specimens irradiated with neutrons at fluences from  $1 \times 10^{16}$  to  $5 \times 10^{19}$  cm<sup>-2</sup> and are attributed to divacancies [17].

Figure 11 shows IRR spectra obtained from three commercial lithium-drifted silicon detectors presumed to be fabricated from specimens of the same silicon crystal. Diode NBS-3S was not irradiated, diode NBS-4S was irradiated with 1.9-MeV protons to a fluence of  $1 \times 10^{14}$  cm<sup>-2</sup> incident on the *p*-contact, and diode NBS-5S was irradiated with 1.5-MeV electrons to a fluence of approximately  $3 \times 10^{13}$  cm<sup>-2</sup> incident on the *p*-contact.

The spectra of diodes NBS-3S and NBS-4S are similar as might be expected since damage caused by 1.9-MeV protons should be localized in the contact region and not in the compensated region of the device. As in the case of NBS-6S (figure 10), the main features are observed at 0.77 and 0.86 eV, and 1.03 eV. The IRR spectrum of the electron-irradiated specimen, diode NBS-5S, shows features at 0.99, and 0.90 eV as well as those at 0.93, 0.86, and 0.77 eV observed in the other silicon diodes, and attributed to divancies after electron irradiation [18]. In the literature, a level located 0.18 eV below the conduction band (0.99 eV) arising from the vacancy-oxygen complex has been reported after neutron- and gamma-irradiation [19,20], while a level 0.27 eV above the valence (0.90 eV) may be associated with lithium precipitates [21].

Since the commercial lithium-drifted silicon detectors used in this study had gold *p*-contacts, approximately 15 to 20 nm thick, through which the infrared radiation must pass, it was necessary to determine what effects, if any, this thin contact had on the measurement of IRR. The infrared transmission of a 0.14-mm thick silicon filter, the thickness used in the measurement of the IRR of silicon detectors, was measured using a thermocouple detector both before and after evaporation of approximately 15 nm of gold onto one side of the filter. No effect was observed in the spectral distribution of the radiation; however, the overall transmission was reduced by a factor of about three as compared to the uncoated filter.

## 6. IDENTIFICATION OF ENERGY LEVELS

In connection with a comprehensive study of methods for the evaluation of germanium suitable for use in Ge(Li) detectors, 85 germanium specimens were collected between 1967 and 1973. Most of these had been rejected for use in the fabrication of high-quality Ge(Li) detectors. Infrared response spectra from 55 of these specimens were identified as to spectrum type; the remaining specimens were of insufficient thickness to permit the fabrication of diodes, were damaged during processing, or yielded IRR spectra whose type could not be identified due to excess noise.

In early IRR measurements, good agreement had been found between energy levels determined from the energies of IRR spectral features and energy levels arising from radiation damage experiments in germanium [3]. However, at that time no attempt was made to distinguish whether features seen in IRR measurements were associated with levels in the upper or in the lower half of the forbidden energy gap. If the various levels observed in IRR spectra could be uniquely identified based on data in the technical literature, and thus linked to a specific crystalline defect, then it might be possible for the crystal grower to identify the source of the defect in the crystal growth procedure. If corrective action could be taken, the quality of the crystal could be upgraded based on the IRR data.

## 6.1 ENERGY LEVELS IN GERMANIUM

After a review of the literature concerning energy levels resulting from radiation or thermal damage in germanium as measured either by photoconductivity or Hall effect [13, 23-46], an attempt was made to link features in the IRR spectra specifically with energy levels observed in the literature [22]. The results are shown in figure 12. From the data published on fast neutron, proton, gamma ray, fast electron, and thermal damage, etc., the summary of energy levels shown in column B was obtained. The shaded bars indicate the energy range of levels for which there were some discrepancy in reported energy but which appeared to arise from the same center. In column A are shown energy levels resulting from IRR measurements of diode NBS 83-3. In this case each energy level appears only once in the scheme; the level was placed at the appropriate energy either below the conduction band edge or above the valence band edge using the levels shown in column B as the basis for comparison. In the majority of cases, a feature observed in the IRR spectrum can be linked uniquely on the basis of energy with a level or band of levels obtained from the summary of the results reported in the literature.

The energy level located 0.18 eV above the valence band (observed at an energy of about 0.54 eV in IRR spectra) is reported to arise specifically from the divacancy-lithium (VVLi) complex and thus should not be observed in lithium-free germanium [38, 46]. Comparison of the IRR spectra obtained from a lithium-drifted diode, NBS 83-3, and from a diode fabricated from high-purity germanium (without lithium compensation), NBS-112, confirms this expectation. The spectrum of NBS 83-3 exhibits a feature at 0.54 eV, but the spectrum of NBS-112 does not.

It is possible to make some specific statements, on the basis of IRR measurements, with regard to the nature of trapping centers in Ge(Li) detectors. Table 4 summarizes the data on the two IRR spectrum types covering detectors that exhibit hole or electron trapping.

Table 4 - Energy Levels in Ge(Li) Detectors Exhibiting Trapping

Spectrum Type <sup>a</sup>	Carrier Trapped	Level (eV)	Nature of Energy Level <sup>b</sup>	Reference
(2)	hole	$E_c - 0.09$	VO complex	[33]
		$E_v + 0.11$	VVLiO complex	
(5)	electron	$E_v + 0.07$	VVLi complex	[41, 51]
		$E_c - 0.09$	VO complex	[33]
		$E_v + 0.11$	VVLiO complex	[44]
		$E_c - 0.21$	VVLiO complex	[44]

<sup>a</sup> as shown in figure 9

<sup>b</sup> V - vacancy, VV - divancy, Li - lithium, O - oxygen

Work on growing high purity germanium indicates that residual oxygen creates charge trapping centers in this material [54]. Thus the assignment of  $\text{LiO}^+$  as the donor species in those levels thought to arise from VVD complexes ( $E_v + 0.11$  eV and  $E_c - 0.21$  eV [46]) seems reasonable. That the main electron trap in Ge(Li) detectors must lie deeper than 0.175 eV [55], appears to point to the  $E_c - 0.21$  eV level which is not observed in hole-trapping crystals.

## 6.2 ENERGY LEVELS IN SILICON

The energy level scheme in figure 13 is a summary of the state of the IRR measurements on radiation-damaged, lithium-drifted silicon nuclear radiation detectors. As in the case of germanium, energy levels reported in the literature [17,18,20,47,50-53] are listed in column B, while energy levels observed in IRR measurements are listed in column A. Tentative identification of IRR-detected levels with corresponding levels reported in the literature has been made previously [6].

## 7. CONCLUSIONS

It has been demonstrated that the IRR technique can be used to qualitatively detect and identify impurities and defects in germanium and silicon with a high degree of sensitivity. In the case of lithium-drifted nuclear radiation detectors, the technique can be used as a predictor of crystal suitability for detector use early in the fabrication process. Similarly, the results of such measurements regarding the presence of certain types of defects in germanium and silicon single crystals should be useful to the crystal grower to better control the growing process.

Given suitable sources of optical radiation, the IRR technique should be applicable to a wide range of semiconductor materials from which diodes can be fabricated. In the case of discrete microelectronic devices (transistors and diodes) the technique might be extended to studies of impurities and defects. This would be useful in analyzing device failure and, in particular, radiation damage effects.

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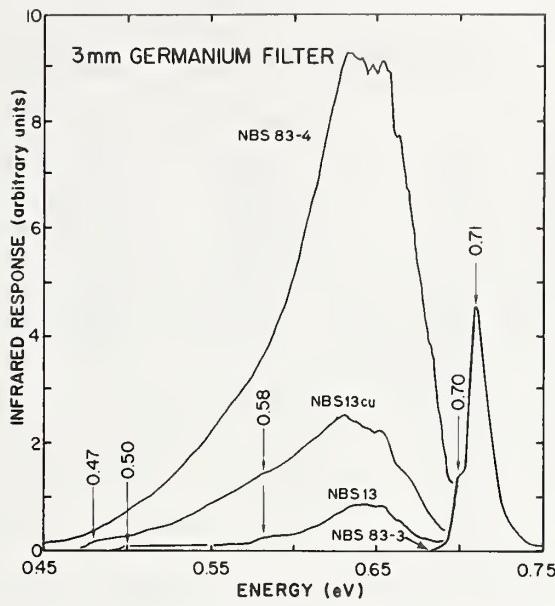


Figure 1. Infrared response obtained using a 3-mm-thick germanium filter. The spectra have been plotted so that the bandedge response peaks of each specimen (at approximately 0.71 eV) overlap. In order to observe a measurable infrared response below the bandedge peak from NBS 83-3, the signal sensitivity level would have to have been increased by a factor of approximately 200. Specimen temperature was approximately 100 K [2].

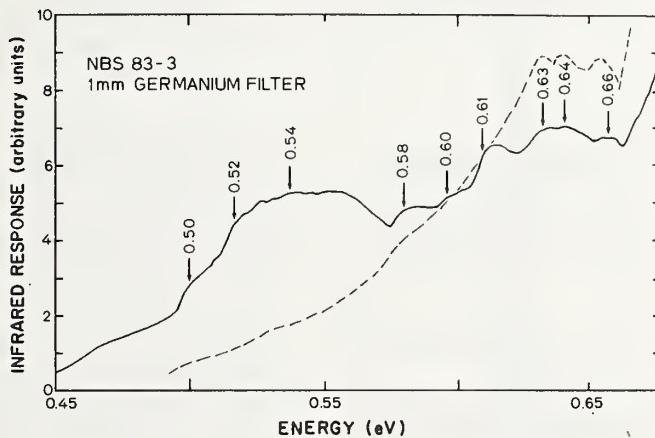


Figure 2. Infrared-response spectrum of NBS 83-3 obtained using a 1-mm-thick germanium filter. The dashed curve is that obtained using the 3-mm-thick germanium filter at an enhanced signal sensitivity. Specimen temperature is approximately 100 K [2].

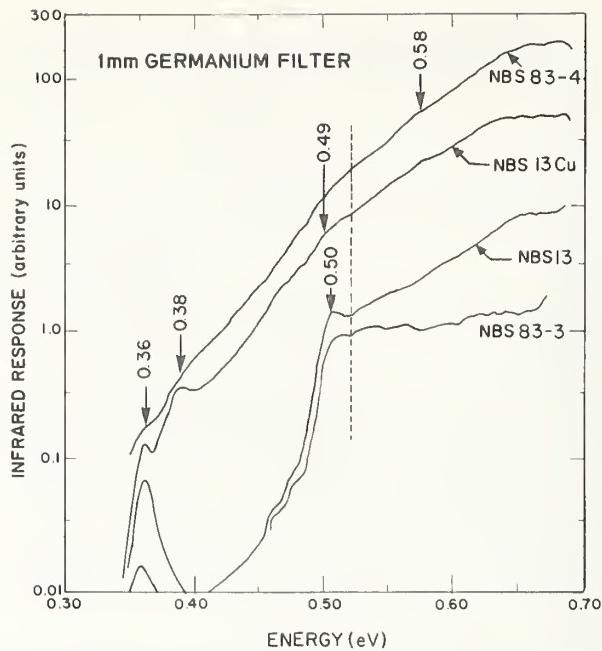


Figure 3. Infrared-response spectra obtained using a 1-mm-thick filter window in the incident photon energy range 0.30 to 0.70 eV. (The spectra are plotted so that the levels of the minimum detectable signal coincide. To the right of the dashed line a 640-line/mm grating was employed; to the left 240 line/mm.) Specimen temperature was about 100 K [2].

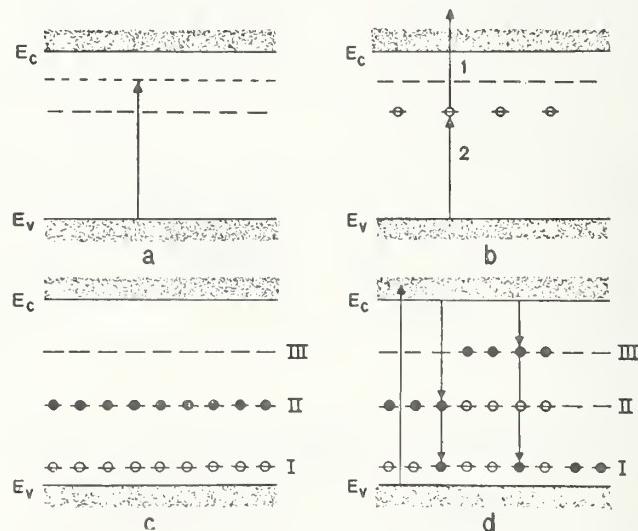


Figure 4. Representations of mechanisms that might yield a photovoltage in *p-i-n* diode: a) transition from valence band to unfilled level; b) double-optical transition; c) the equilibrium conditions for the charge exchange process, and d) the transitions for the charge exchange process [6].

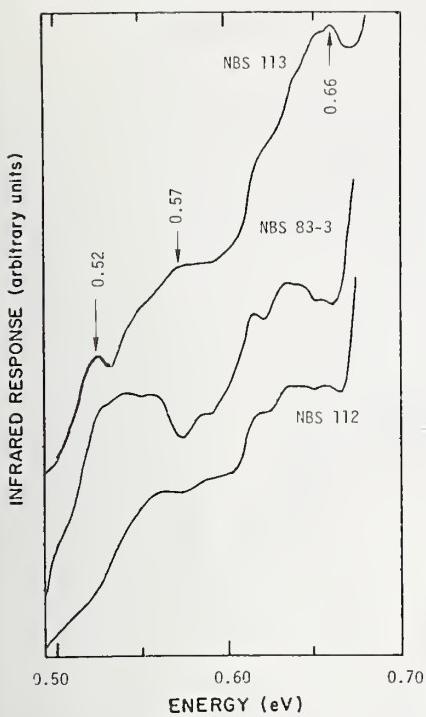


Figure 5. IRR spectra of two high purity germanium diodes and NBS 83-3, shown for comparison, obtained using a 1-mm thick germanium filter [9].

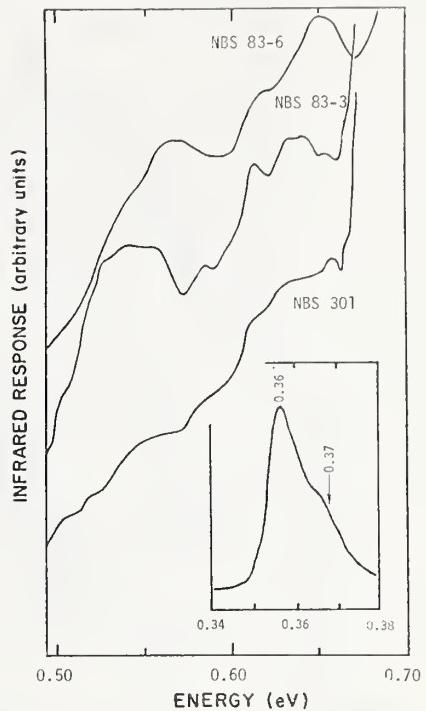


Figure 6. IRR spectra of three lithium-drifted germanium diodes obtained using a 1-mm thick germanium filter. Inset shows a portion of the spectrum of NBS 301 [9].

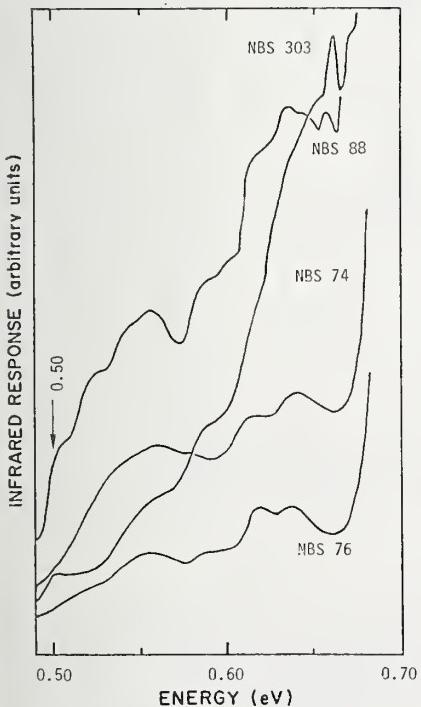


Figure 7. IRR spectra obtained using a 1-mm thick germanium filter from two lithium-drifted germanium diodes that exhibit electron trapping (NBS 303 and NBS 83-8) and two diodes that exhibit hole trapping (NBS 74 and NBS 76) [9].

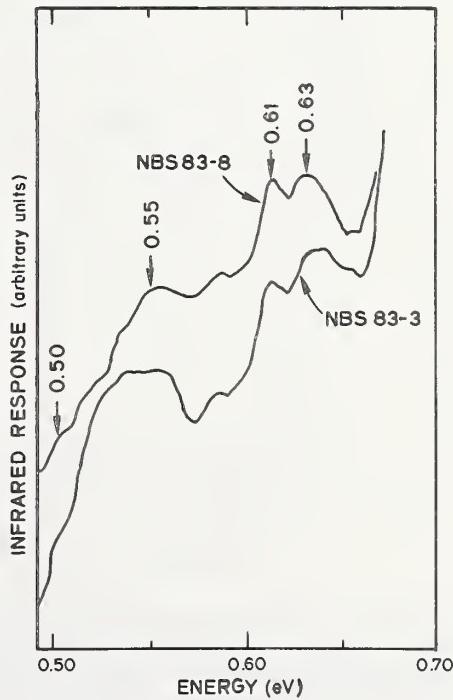


Figure 8. Infrared response spectra of two germanium gamma-ray detectors [12].

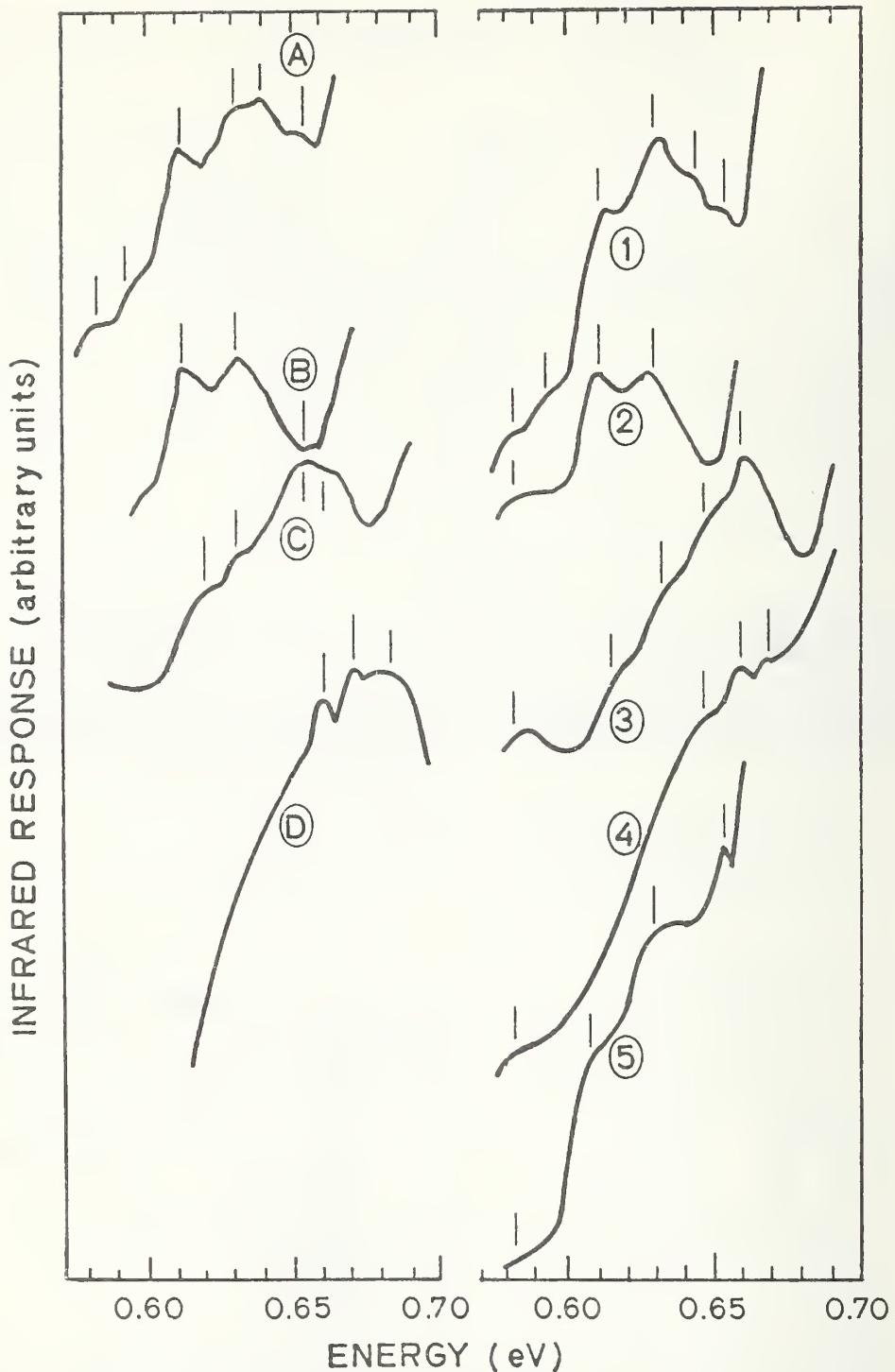


Figure 9. Infrared response spectra obtained from five lithium-drifted germanium diodes fabricated from crystals from five different sources [(1) - (5)] and four diodes fabricated from specimens of another crystal treated in known manners [(A) - (D)]. (Spectral features of interest as indicated by short vertical lines are identified in table 1. The diodes are identified in table 2.) [14].

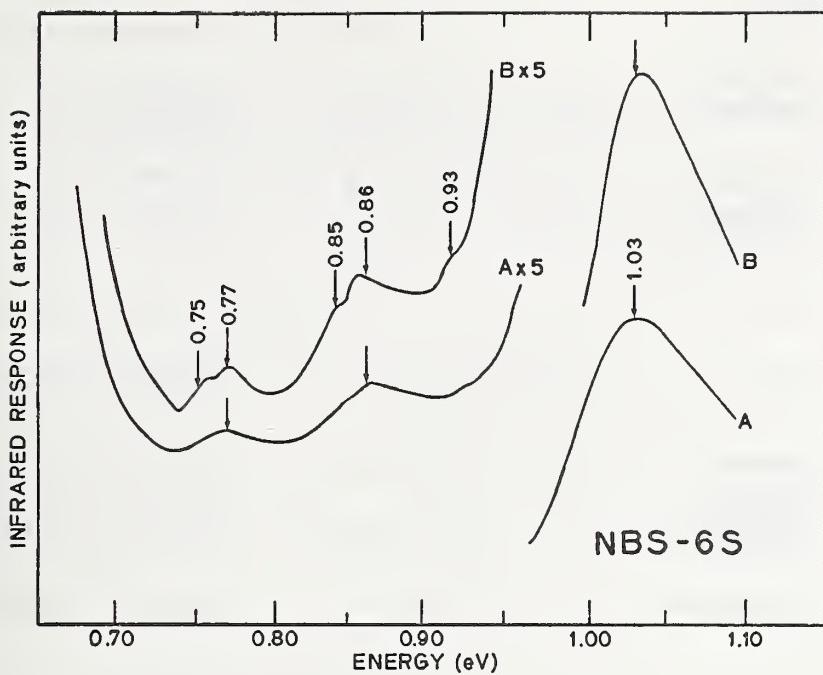


Figure 10. Infrared response spectra of a commercial lithium-drifted silicon detector obtained before (A) and after (B) irradiation with fast neutrons [9].

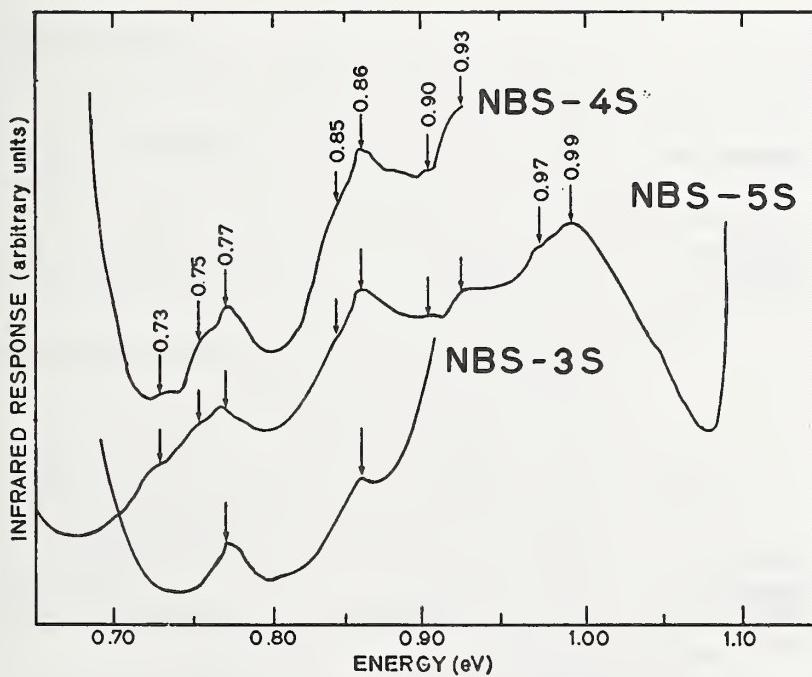


Figure 11. Infrared response spectra of three commercial lithium-drifted silicon detectors. (Large peaks, similar to that in the spectrum of NBS-6S shown in figure 10, occur at 1.03 eV in the spectra of NBS-3S and NBS-4S. These are not shown because they exceed the scale of the figure.) [9].

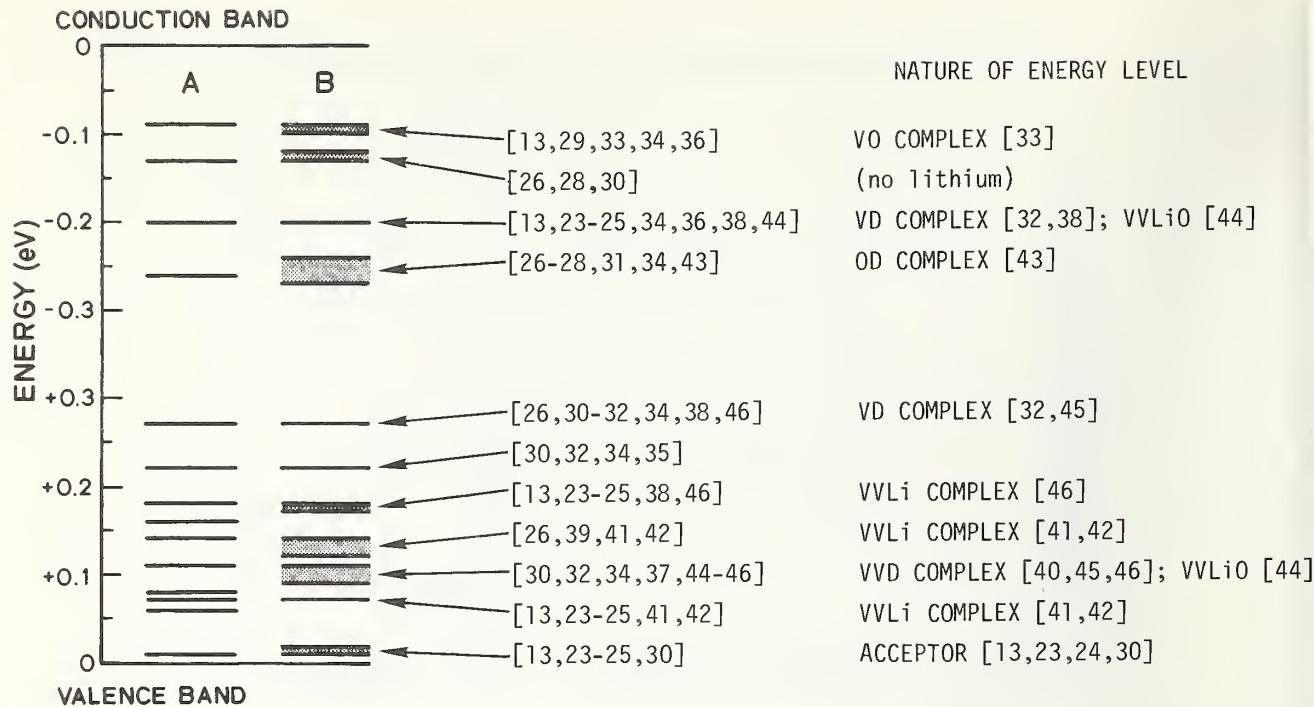


Figure 12. Energy level scheme comparing features detected in IRR measurements on germanium diodes (A) with levels resulting from radiation or thermal damage (B). References are given in brackets. Symbols used: V-vacancy, VV-divacancy, O-oxygen, D-donor, Li-lithium [26].

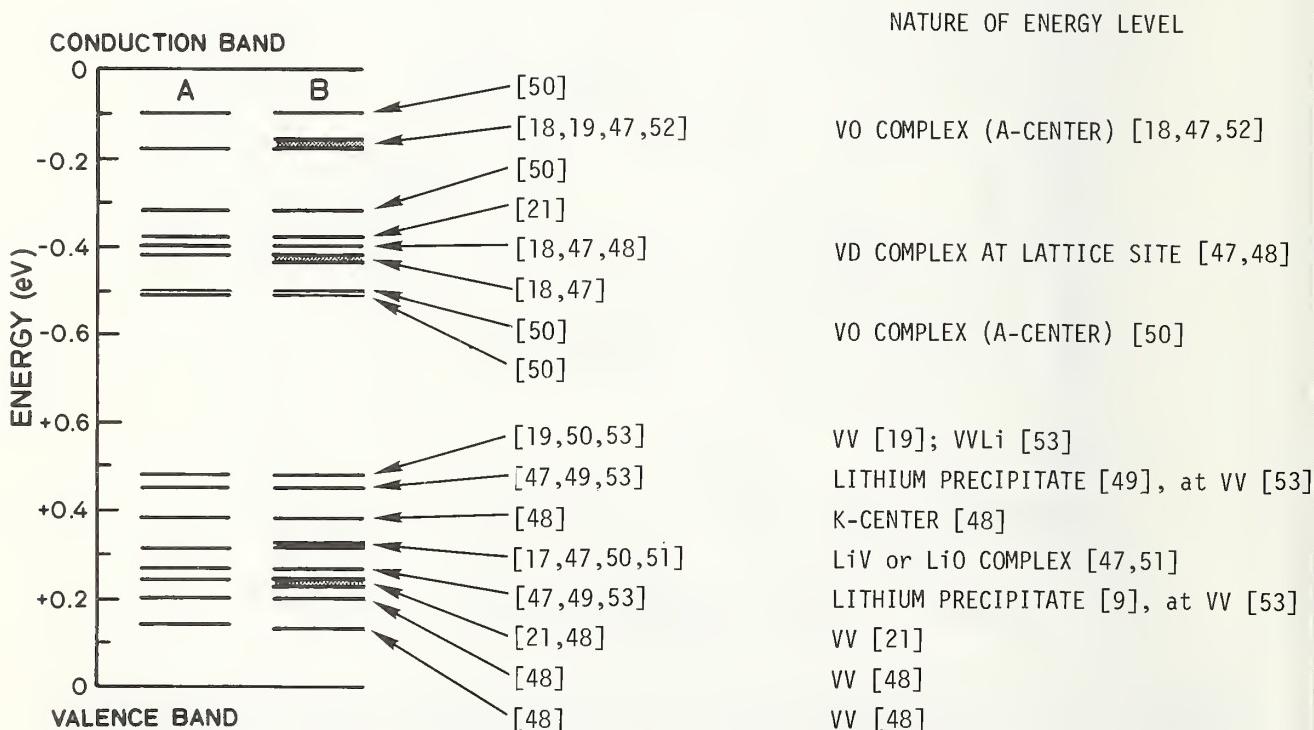


Figure 13. Energy level scheme comparing features detected in IRR measurements on silicon diodes (A) with levels resulting from radiation damage (B). References are given in brackets. Symbols used: V-vacancy, VV-divacancy, O-oxygen, D-donor, Li-lithium [26].

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## SUPPLEMENTARY NOTES

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ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

An infrared response (IRR) technique was evaluated for its utility in qualifying germanium for radiation detector use. Because of several improvements in the sensitivity and interpretation of the technique made during the evaluation, it was possible to observe a number of discrete energy levels lying within the forbidden energy gap of germanium which had passed unobserved in previous studies. These levels correlate with the type of defects and vacancies introduced by radiation damage into germanium as measured using such techniques as photoconductivity and Hall effect measurements after irradiation. Furthermore, the improved infrared response measurement method was used to identify impurities, such as copper, gold, and iron, and dislocations resulting from heat treatments in germanium. A major advance was made when it was determined that the IRR spectra could be grouped into five distinct types on the basis of spectral features observed in the energy range from 0.6 to 0.7 eV. One of the spectrum types represented crystals from which good quality detectors could be fabricated; the other four represented crystals that yielded poorer quality detectors due to carrier trapping, or crystals that presented problems such as low lithium drift mobility in detector fabrication. Three of the four spectrum types representative of poor crystal quality could be duplicated by suitably degrading specimens of a good quality crystal. The material and detector characteristics of crystals within each spectrum type were found to be similar.

KEY WORDS (six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)

Carrier trapping; gamma-ray detector; germanium; Ge(Li) detector; infrared response silicon.

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